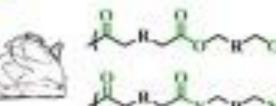


Lipids (saponifiable and nonsaponifiable)



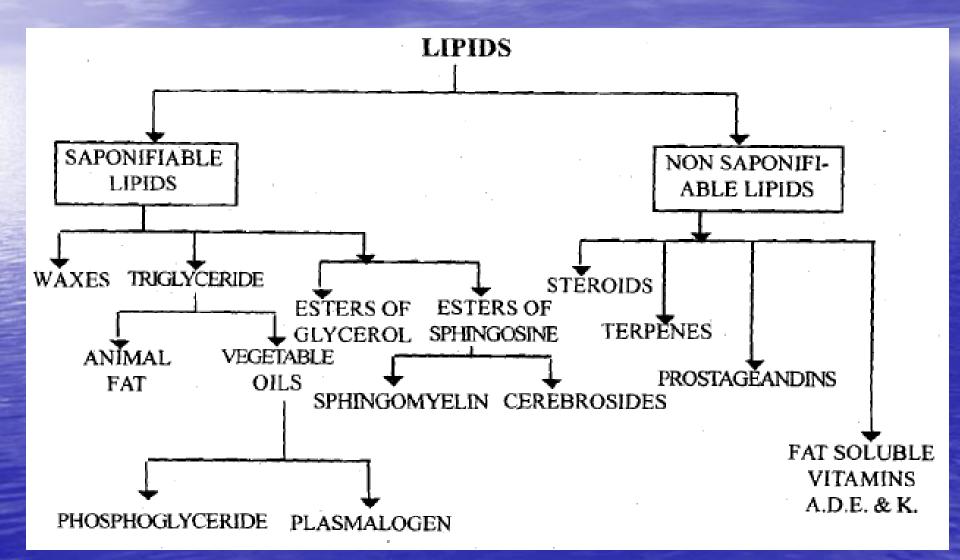
Biomass based polymers and products



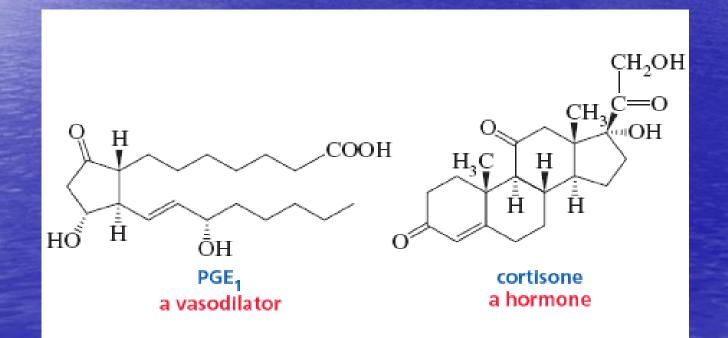
Lipids

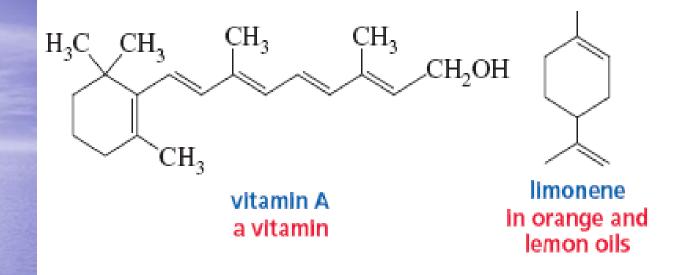
Lipids differ from the other classes of naturally occurring biomolecules (carbohydrates, proteins, and nucleic acids), they are more soluble in nonor weakly polar solvents (diethyl ether, hexane, dichloromethane) than in water.

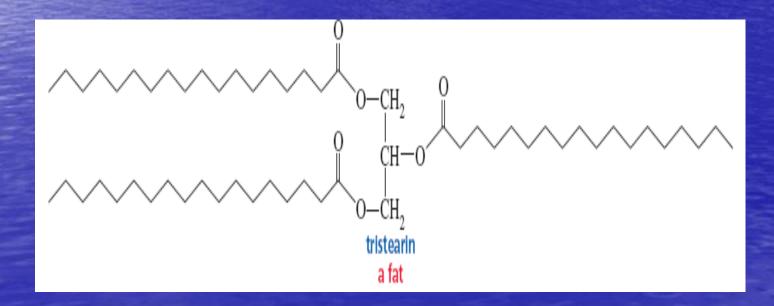
Classification of lipids



Lipids are organic compounds, found in living organisms, that are soluble in nonpolar organic solvents. Because compounds are classified as lipids on the basis of a physical property— their solubility in an organic solvent rather than as a result of their structures, lipids have a variety of structures and functions, as the following examples illustrate:







Functions of lipids – The most important role of lipids is as a fuel.

 Some compounds derived from lipids are important building blocks of biologically active materials; e.g. acetic acid can be used by the body to synthesize cholesterol and related compounds (hormones).

 Lipoproteins are constituents of cell walls. The lipids present in lipoproteins constituting the cell walls are phospholipids. Since lipids are water insoluble they act as ideal barrier for preventing water soluble materials from passing freely between the intraand extra-cellular fluids.

 One more important function of dietary lipids is that of supplying the essential fatty acids ,there are several functions

Functions of lipids

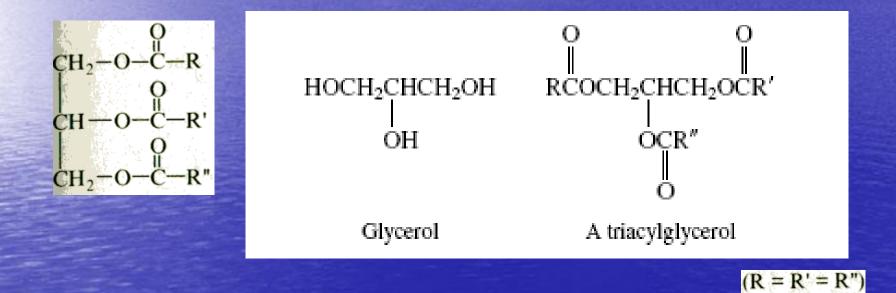
1. The most important role of lipids is as a fuel.

 Fatty acids with their flexible backbones can be stored in a much more compact form than the highly spatially oriented and rigid glycogen structure. Thus fat storage provides economy in both weight and space. Fat storage is an excellent form of energy.

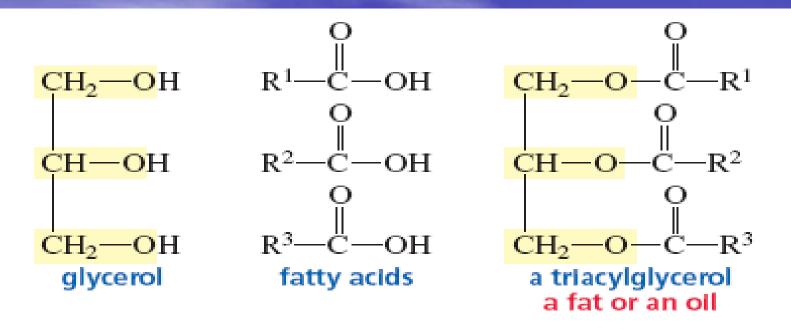
 As it is insoluble in water, it has been carried to the fat depots by the specialised transport proteins in the plasma.

– It remains as a stable and fixed reserve of energy until mobilized by enzymes which hydrolyse it to glycerol and fatty acids. The enzymes are under the control of various hormones and are activated under conditions where the body is involved in increased energy expenditure.

-Fat may also provide padding to protect the internal organs. Brain and nervous tissue are rich in certain lipids, a fact which indicates the importance of these compounds to life. **Fats and oils** are naturally occurring mixtures of *triacylglycerols*, also called *triglycerides*. They differ in that fats are solids at room temperature and oils are liquids. We generally ignore this distinction and refer to both groups as fats. Triacylglycerols are built on a glycerol framework.



Simple triacylglycerines include similar fatty acids mixed – different.



Triacylglycerols that are solids or semisolids at room temperature are called fats. Fats are usually obtained from animals and are composed largely of triacylglycerols with either saturated fatty acids or fatty acids with only one double bond. The saturated fatty acid tails pack closely together, giving the triacylglycerols relatively high melting points, causing them to be solids at room temperature. Liquid triacylglycerols are called oils. Oils typically come from plant products such as corn, soybeans, olives, and peanuts. They are composed primarily of triacylglycerols with unsaturated fatty acids that cannot pack tightly together. Consequently, they have relatively low melting points, causing them to be liquids at room temperature.

Structural formula	Systematic name	Common name
Saturated fatty acids		
CH ₃ (CH ₂) ₁₀ COOH CH ₃ (CH ₂) ₁₂ COOH CH ₃ (CH ₂) ₁₄ COOH CH ₃ (CH ₂) ₁₆ COOH CH ₃ (CH ₂) ₁₈ COOH	Dodecanoic acid Tetradecanoic acid Hexadecanoic acid Octadecanoic acid Icosanoic acid	Lauric acid Myristic acid Palmitic acid Stearic acid Arachidic acid
Unsaturated fatty acids		
$CH_3(CH_2)_7CH = CH(CH_2)_7COOH$ $CH_3(CH_2)_4CH = CH(CH_2CH = CH(CH_2)_7COOH$	(Z)-9-Octadecenoic acid (9Z,12Z)-9,12- Octadecadienoic acid	Oleic acid Linoleic acid
$CH_3CH_2CH = CHCH_2CH = CH(CH_2)_7COOH$	(9Z,12Z,15Z)-9,12,15- Octadecatrienoic acid	Linolenic acid
CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CHCH ₂ CH=CH(CH ₂) ₃ COOH	(5Z,8Z,11Z,14Z)- 5,8,11,14- Icosatetraenoic acid	Arachidonic acid

The most widespread fatty acids in natural oils and fats:

Acid	Common name	Source	
Saturated acids			
$H_3C(CH_2)_{14}COOH$	palmitic acid	palm kernel oil	
$H_3C(CH_2)_{16}COOH$	stearic acid	beef fat	
Unsaturated acids			
$H_3C(CH_2)_5CH=CH(CH_2)_7COOH$	palmitoleic acid	palm oil	
$H_3C(CH_2)_7$ CH=CH (CH ₂) ₇ COOH	oleic acid	olive oil	
$H_3C(CH_2)_3$ (CH ₂ CH=CH) (CH ₂) ₇ COOH	linoleic acid	linseed oil	
H_3C (CH ₂ CH=CH) ₃ (CH ₂) ₇ COOH	linolenic acid	linseed oil	

Nomenclature, methods of getting of fats

For simple glycerides the name is made up of the name of the alcohol (glycerol) or its radical (glyceryl) and the name of the acid; or the name of the acid concerned is changed to suffix in. For mixed glycerides, the position and names of the acid groups are specified by Greek letters α , β , α' or by the numerals 1, 2 and 3.

1-lauro-2-palmitostearine

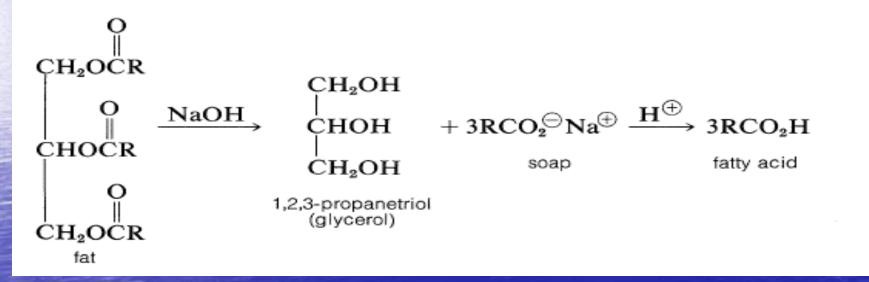
Chemical properties of fats Hydrolysis of a triacylglycerol

Hydrolysis of a triacylglycerol is the reverse of the esterification reaction by which it was formed. Complete hydrolysis of a triacylglycerol molecule always gives one glycerol molecule and three fatty acid molecules as products.

$$\begin{array}{c} CH_{2}-O-C & O \\ | \\ CH_{2}-O-C & O \\ | \\ CH_{2}-O-C & O \\ CH_{2}-O-C & O \\ CH_{2}-O-C & O \\ R \end{array}^{O} + 3 H-O-H \xrightarrow{\text{Steam}}_{H^{2}} CH_{2}-O-H+R'COOH \\ | \\ CH_{2}-O-C & O \\ R \end{array}$$

Chemical properties of fats

1). <u>Hydrolysis of fats with alkali</u> (e.g., sodium hydroxide) yields salts of the fatty acids, and those of the alkali metals, such as sodium or potassium and use as soaps. Another name of this reaction – "saponification":



The solubility of lipids in nonpolar organic solvents results from their significant hydrocarbon component. The hydrocarbon portion of the compound is responsible for its "oiliness" or "fattiness." The word *lipid* comes from the Greek *lipos*, which means "fat."

Characterization of fats. The composition, quality and purity of a given oil or fat is determined by means of a number of physical and chemical tests. The usual physical tests include determination of m, p, specific gravity, viscosity, etc. while the chemical tests include determination of certain values discussed below.

I. Acid number. It is the number of milligrams of potassium hydroxide required to neutralise the free fatty acids in 1g. of the oil or fat. Thus it indicates the amount of free fatty acids present in oil or fat. A high acid value indicates a stale oil or fat stored under improper conditions.

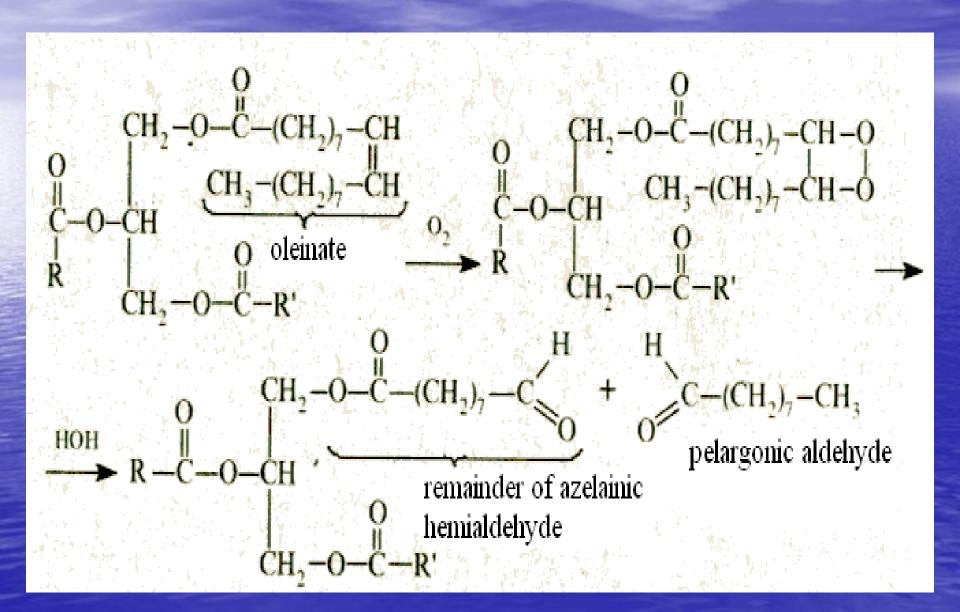
Characterization of fats. The composition, quality and purity of a given oil or fat is determined by means of a number of physical and chemical tests. The usual physical tests include determination of m, p, specific gravity, viscosity, etc. while the chemical tests include determination of certain values discussed below.

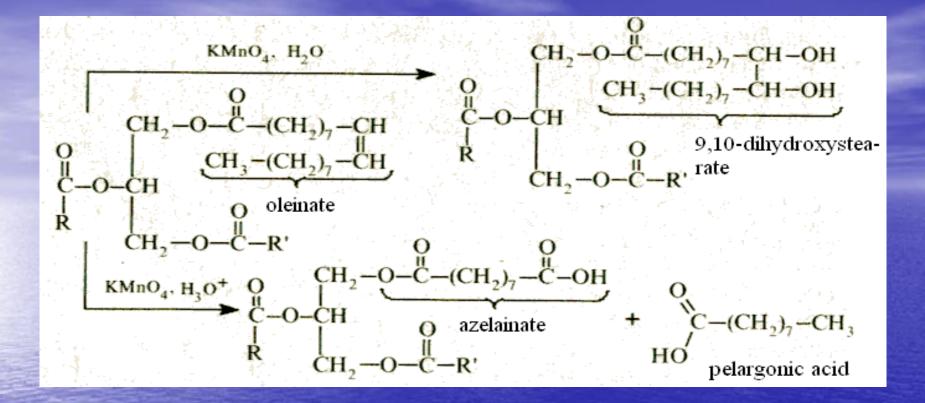
• 2. Saponification number. It is number of milligrams of potassium hydroxide required to completely hydrolysis of I g. of the oil or fat. Thus it is a measure of fatty acids present as esters in a given oil or fat. The saponification value gives an idea about the molecular weight of fat or oil. The saponification number and molecular weight of an oil are inversely proportional to each other; thus high saponification number indicates that the fat is made up of low molecular weight fatty acids and vice versa. It is also helpful in detecting adulteration of a given fat by one of the lower or higher saponfication value.

Characterization of fats. The composition, quality and purity of a given oil or fat is determined by means of a number of physical and chemical tests. The usual physical tests include determination of m, p, specific gravity, viscosity, etc. while the chemical tests include determination of certain values discussed below.

3. Iodine number. It is the number of grams of iodine that combine with 100 g. of oil or fat. It is a measure of the degree of unsaturation of a fat or oil; a high iodine number indicates a high degree of unsaturation of the fatty acids of the fat.

2). Oxidation of fates. Oxidation cases rancidity of fates. During oxidation form aldehydes with short carbon chain.

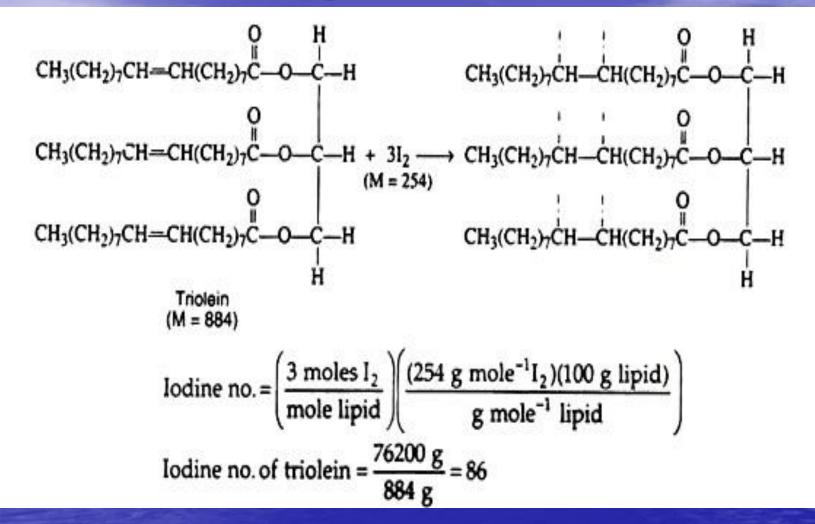




Oxidation at the soft conditions (water solution of KMnO4) cases formation of glycols. At the rigid conditions carbon skeleton destroys with formation of remainders of carbonic acids with shorter carbon chains. Fats, which predominantly contain saturated fatty acids, by oxidation form ketones.

3). Hydrogenation. Margarine is prepared by hydrogenating vegetable oils such as soybean oil and sunflower oil until they have the desired consistency. This process is called "hardening of oils." The hydrogenation reaction must be carefully controlled, however, because reducing all the carbon-carbon double bonds would produce a hard fat with the consistency of beef tallow. Quantity of H2 in grams, which are necessary for hydration of 10kg of fats (hydration number) characterizes unsaturating of fat.

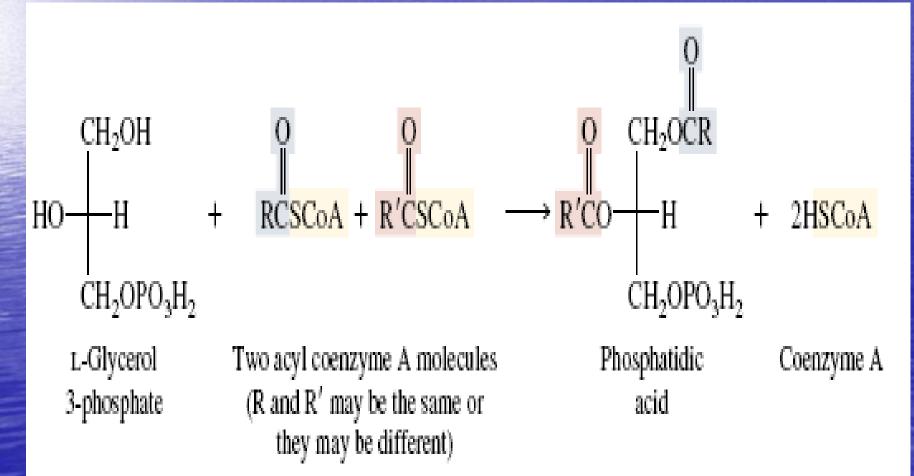
4). Addition of halogens.



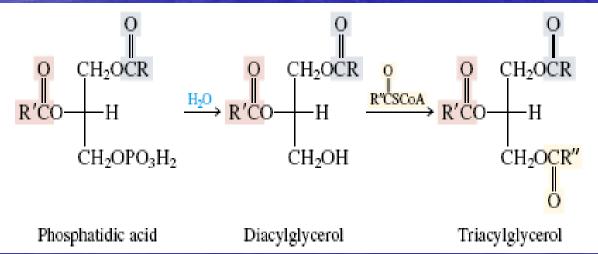
Iodine number for plants fats – 100-200, for animal fats – 25-86, for fish fats – 100-193.

Phospholipids.

Triacylglycerols arise, not by acylation of glycerol itself, but by a sequence of steps in which the first stage is acyl transfer to L-glycerol 3-phosphate. The product of this stage is called a **phosphatidic acid**.



Hydrolysis of the phosphate ester function of the phosphatidic acid gives a diacylglycerol, which then reacts with a third acyl coenzyme A molecule to produce a triacylglycerol. Phosphatidic acids not only are intermediates in the biosynthesis of triacylglycerols but also are biosynthetic precursors of other members of a group of compounds called phosphoglycerides or glycerol phosphatides. Phosphoruscontaining derivatives of lipids are known as **phospholipids**, and phosphoglycerides are one type of phospholipid. One important phospholipid is **phosphatidylcholine**, also called *lecithin*. Phosphatidylcholine is a mixture of diesters of phosphoric acid.

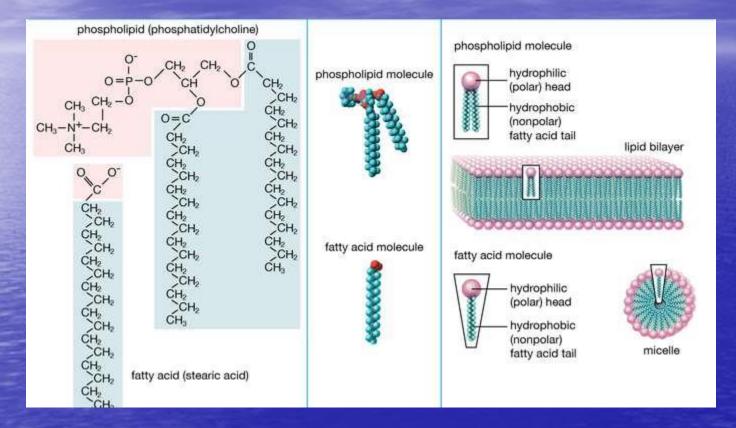


Classification of phospholipids

 \sim

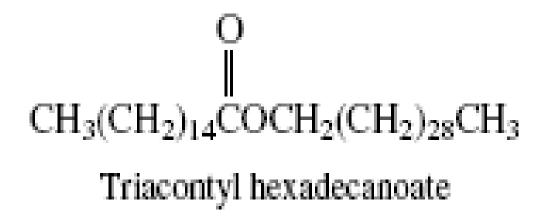
CH2-O-C R CH - O-C R' CH2-O-P-O-	x	
Name of X -	Formula of X	Name of phospholipid
OH		
Water	-H	Phosphatidic acid
Choline	$-CH_2-CH_2-N(CH_3)_3$	Phosphatidylcholine (Lecithin)
Ethanolamine	-CH2-CH2-NH3	Phosphatidylethanolamine (cephalin)
Serine	-CH2-CH2-NH3 COOT	Phosphatidylserine
Glycerol	CH2 - CH - O-H CH2 -O-H	Phosphatidylglycerol

Membrane structure



Waxes

Waxes are water-repelling solids that are part of the protective coatings of a number of living things, including the leaves of plants, the fur of animals, and the feathers of birds. They are usually mixtures of esters in which both the alkyl and acyl group are unbranched and contain a dozen or more carbon atoms. Beeswax, for example, contains the ester triacontyl hexadecanoate as one component of a complex mixture of hydrocarbons, alcohols, and esters.



- Bees wax. It contains esters derived from alcohols having 24

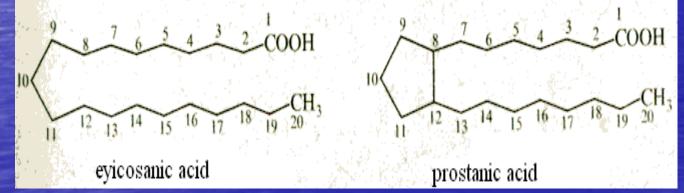
 30 carbon atoms, include palmitate of miricyl alcohol (C30H610H) and n-hexacosanol (C26H530H).

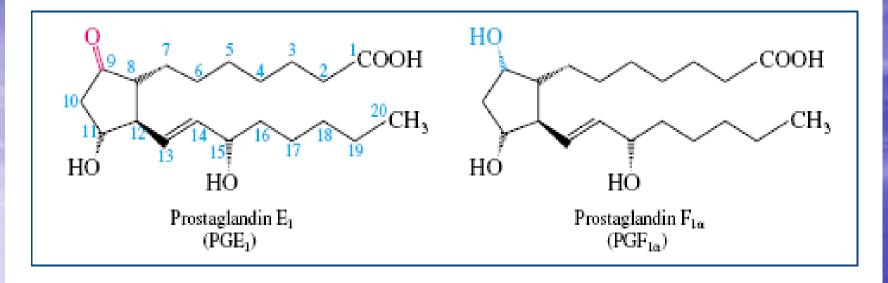
 CH3(CH2)14COOC30H61 CH3 (CH2)14COOC26H53

 miricyl patmitate
 n- hexacosanyl patmitate
- Spermaceti. It is obtained from the head of the sperm whale. It is rich in ester of cetyl alcohol (C16H33OH) and palmitinic acid: CH3 (C H2) 14COOC16H33 - cetyl palmitate
 Spermaceti is used in making of candles.
- Carnauba wax. It is found in the leaves of the carnauba palm of Brazil. It is used as an ingredient in the manufacture of various wax polishes. Because waxes are very inert chemically, they make an excellent protective coating.
- Lanolin or wool wax. It is obtained from wool and is used in making ointments and salves.

Nonsaponifiable lipids

 Prostaglandins – physiologically active substances with biogenic origin, stimulate smooth muscles and lowers blood pressure. All prostaglandins contain carboxyl group and 20 carbon atoms in molecule, they are derivatives of eyicosanic acid.





All the prostaglandins are 20-carbon carboxylic acids and contain a cyclopentane ring. All have hydroxyl groups at C-11 and C-15 (for the numbering of the positions in prostaglandins). Prostaglandins belonging to the F series have an additional hydroxyl group at C-9, and a carbonyl function is present at this position in the various PGEs. The subscript numerals in their abbreviated names indicate the number of double bonds. Prostaglandins are believed to arise from unsaturated C20-carboxylic acids such as arachidonic acid. Mammals cannot biosynthesize arachidonic acid directly.



Sune K. Bergström



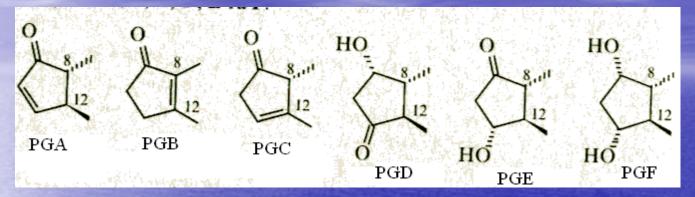


John R. Vane

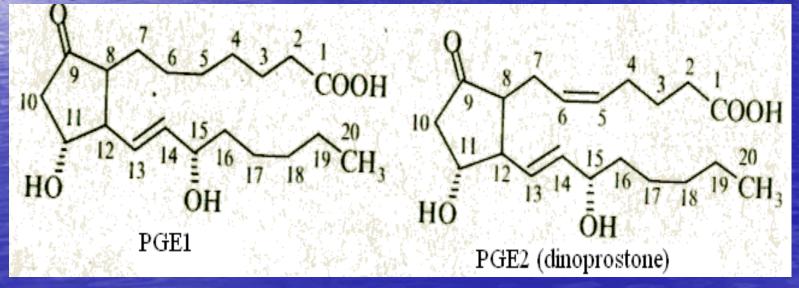
Much of the fundamental work on prostaglandins and related compounds was carried out by Sune Bergström and Bengt Samuelsson of the Karolinska Institute (Sweden) and by Sir John Vane of the Wellcome Foundation (Great Britain). These three shared the Nobel Prize for physiology or medicine in 1982.

Bengt I. Samuelsson

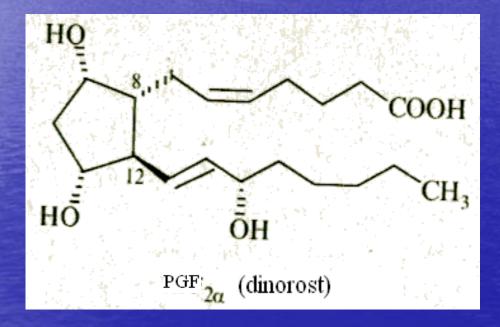
Prostaglandins have cyclopentane ring. According to allocation of double bonds in fivemember cycle and side chains prostaglandins marked by litters A, B, C, D, E and F.



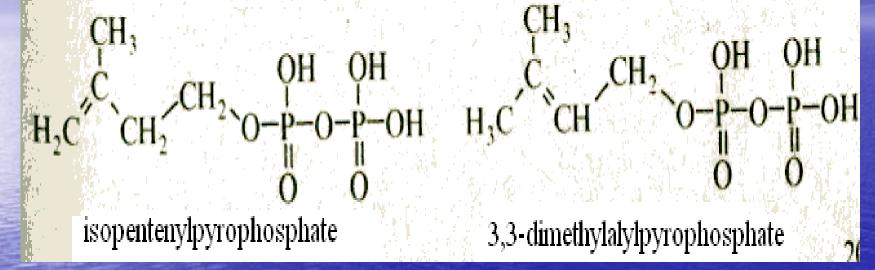
According to the number of double bonds in side chains every group of prostaglandins divided on series that marked as indexes.



In the names of prostaglandins orientation of hydroxyl group in location 9 according to the carbon chain at C8 mark α or β . α – means cis-configuration, β – trance.



Isoprenoides – products of isoprene сн.=с(сн.) - сн=сн. transformation. Some vitamins and hormones have isoprenoides structure.



Isoprenoides includes terpens, carotinoids and steroids

$$CH_{2} = C - CH = CH_{2} + [H] - CH = C - CH = CH_{2}$$

isoprene
$$CH_{2} = C - CH_{2} - CH_{3} - CH_{2} - CH_{$$

Terpenes and terpenoids. Terpene biosynthesis.

A terpene is a naturally occurring hydrocarbon based on combinations of the isoprene unit. Terpenoids are compounds related to terpenes, which may include some oxygencontaining derivatives (alcohols, aldehydes and ketones).



Functions of terpenes

Terpenes play a vital role in plants:attract pollinators,

 cause a strong reaction to repel predators, such as insects or foraging animals.

 protective role in the plant, helping the plant to recover from damage;

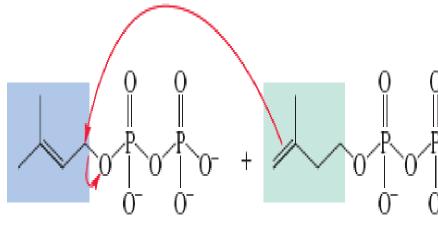
 plant's immune system to keep away infectious germs. The name "terpene" is derived from the word "turpentine". In addition to their roles as end-products in many organisms, terpenes are major biosynthetic building blocks within nearly every living creature.

When terpenes are modified chemically, such as by oxidation or rearrangement of the carbon skeleton, the resulting compounds are generally referred to as terpenoids.

Terpenes and terpenoids are the primary constituents of the essential oils of many types of plants and flowers.

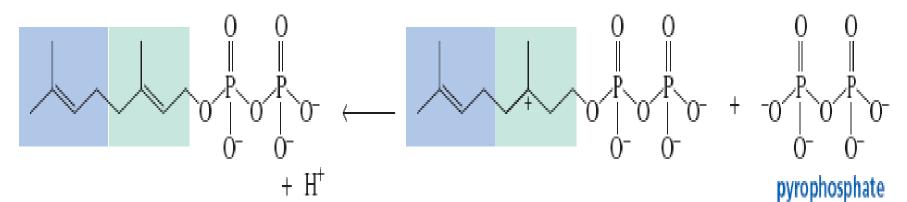


Terpene biosynthesis.

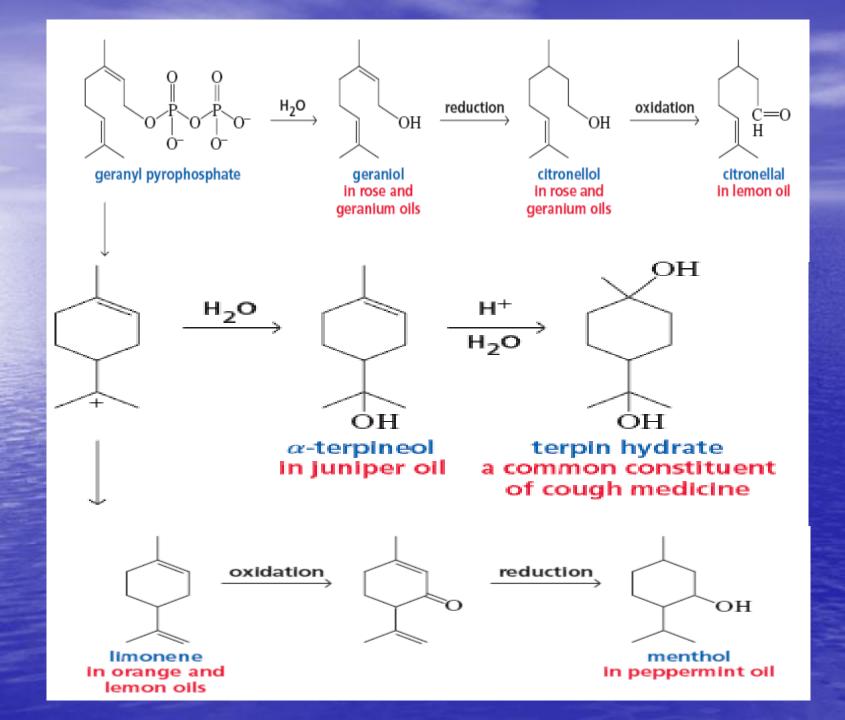


dimethylallyl pyrophosphate





geranyl pyrophosphate





 Terpenes are natural products that are structurally related to isoprene (C₅H₈). CH₃ or $H_2C = CH = CH_2$ Isoprene (2-methyl-1,3-butadiene)

Terpenoids are oxygen-containing terpenes

The Isoprene Unit

The isoprene units are joined "head-totail."





tail hea

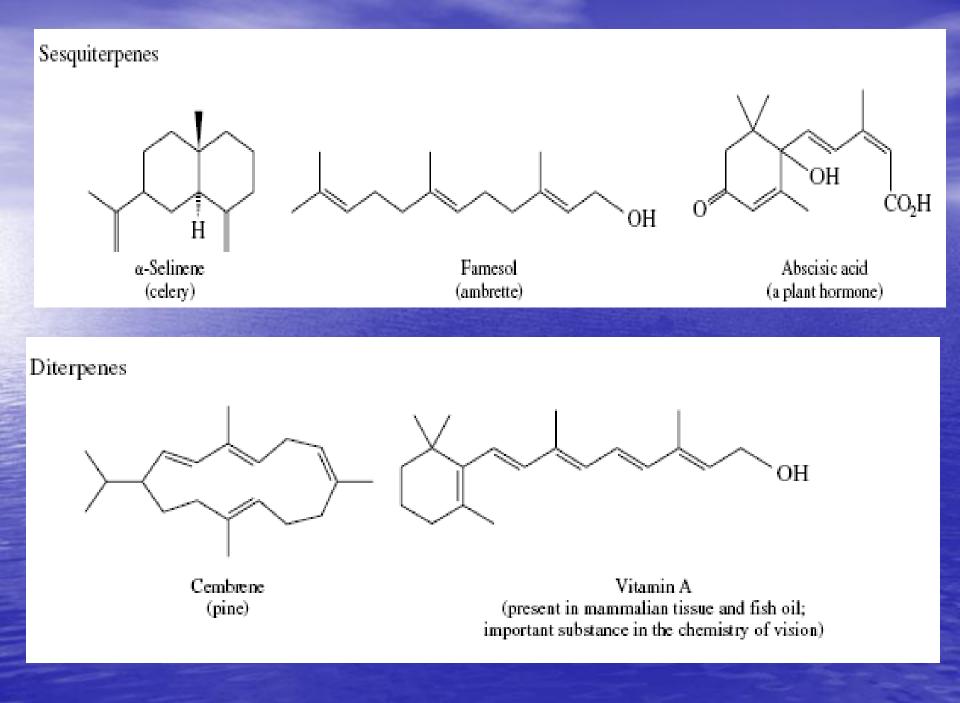
tail

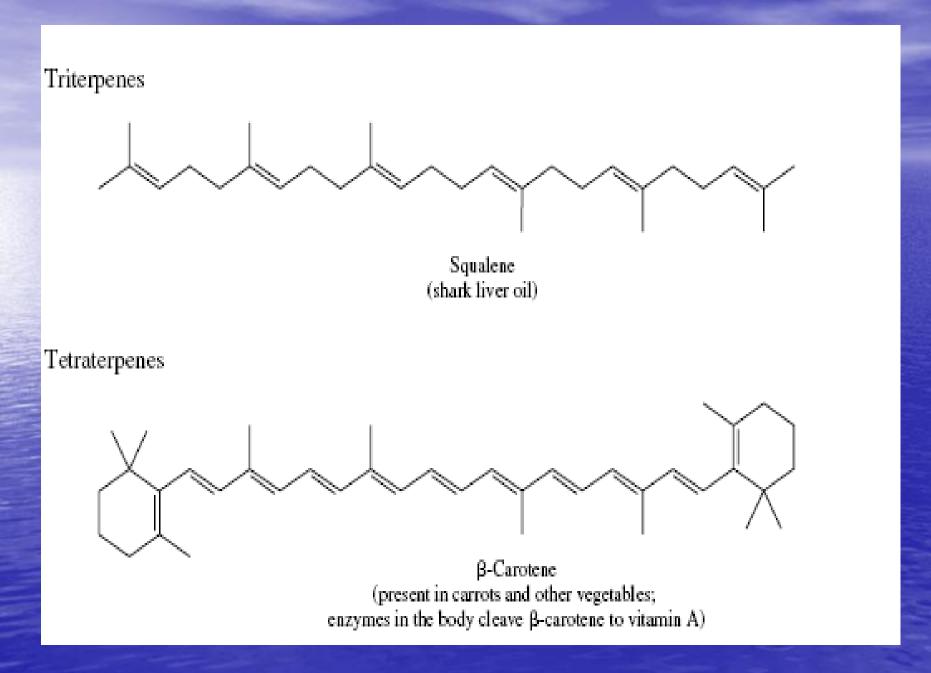
Otto Wallach

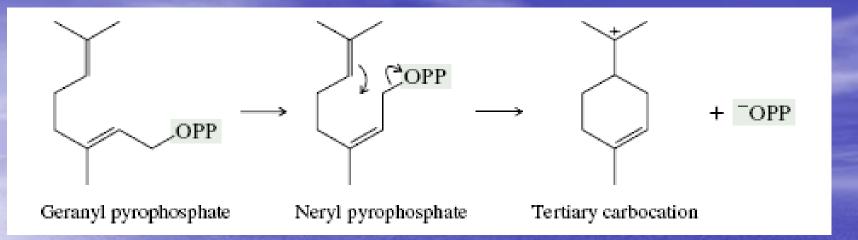
Mean ...to the class now called isoprenoids. Wallach's work laid the scientific basis the modern perfume industry....

Classification of Terpenes

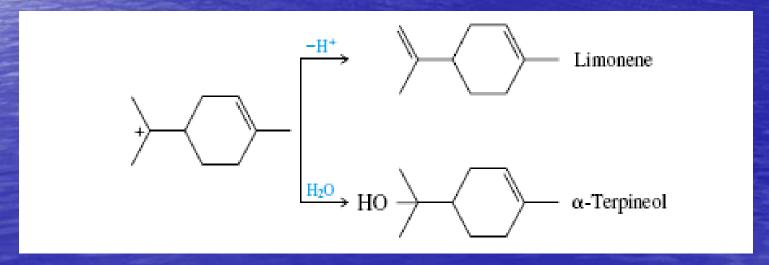
Number of carbon atoms Class Monoterpene 10 Sesquiterpene 15 20 Diterpene Sesterpene 25 Triterpene 30 Tetraterpene 40







Loss of a proton from the tertiary carbocation formed in this step gives *limonene*, an abundant natural product found in many citrus fruits. Capture of the carbocation by water gives *-terpineol*, also a known natural product.



Monoterpens

The monoterpenes are isolated from their natural sources by distillation of the plant matter with steam. They are volatile oils, less dense than water, and have normal <u>boiling points</u> in the range of 150 to 185 °C (300 to 365 °F). Purification is usually achieved by fractional distillation at reduced pressures or by regeneration from a crystalline derivative. Acyclic monoterpene hydrocarbons are few in number, but their oxygenated derivatives are more widespread in nature and of greater importance.

They are the terpenes that have been known for several centuries as components of the fragrant oils obtained from leaves, flowers and fruits. Monoterpenes, with sesquiterpenes, are the main constituents of essential oils.

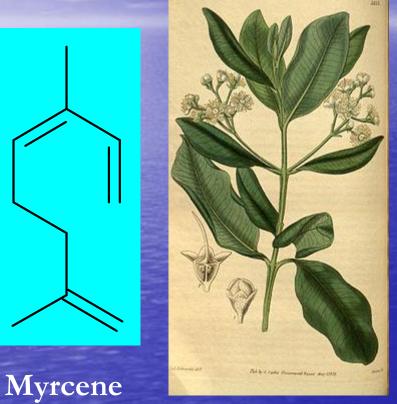
Monoterpens

In the basis of carbon skeleton acyclic monoterpens are structures of isoprene isomeric dimers: myrcene and ocimene.

myrcene; 7-methyl-3-methyleneoctadiene ocimene;

3,7-dimethyloctatriene

Monoterpenes (C₅H₈)₂



Ocimene

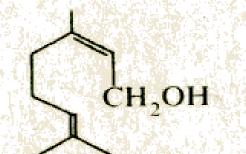
Ocimum basilicum

Myrcia acris



Monoterpens

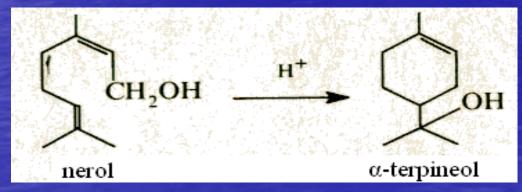
Geraniol and nerol alcohols are derivatives of carbohydrates monoterpens. Geraniol has cis-form and nerol – trance-form.



geraniol; cis-3,7-dimethyloctadiene-2,6-ol-1

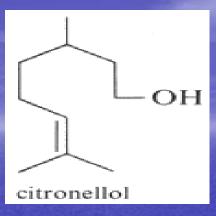
CH,OH

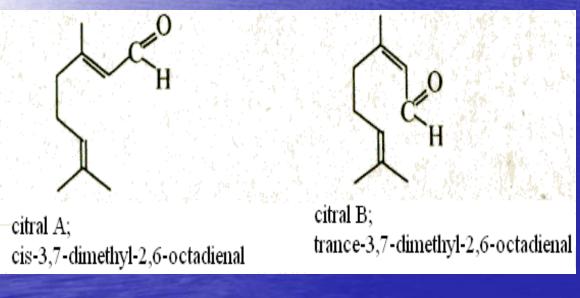
nerol; trance-3,7-dimethyloctadiene-2,6-ol-1



Monoterpens

Geraniol and citral present in ether oils, especially in citric oil. They are pheromones.

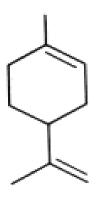






Monocyclic monoterpenes

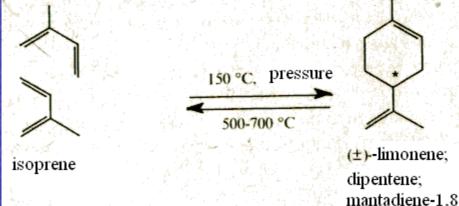
They are derived from cyclohexane with an isopropyl substituent. The most important members are limonene and methane.



limonene

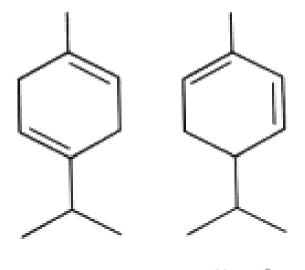


Limonene (dipentene) can be obtained by isoprene isomerisation with heating to 150 C in soldered ampoule. At 500-700 C reverse processes takes place.



Monocyclic monoterpenes

They are derived from cyclohexane with an isopropyl substituent. The most important members are limonene and methane.



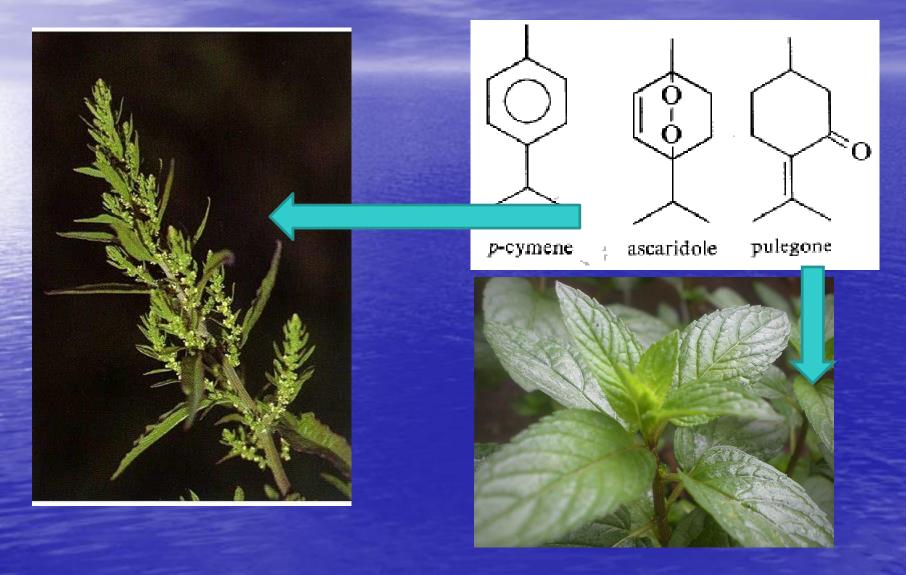
γ-terpinene α-phellandrene



EUCALYPTUS Eucalyptus radiata My life is filled with unlimited possibilities.

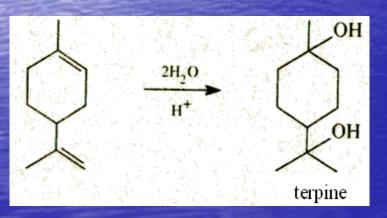
Monocyclic monoterpenes

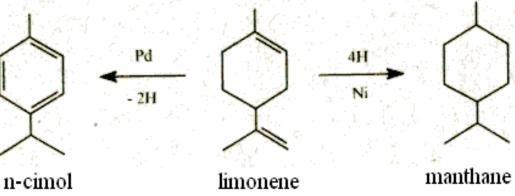
They are derived from cyclohexane with an isopropyl substituent. The most important members are limonene and methane.

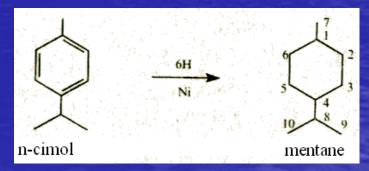


Chemical reactions of monoterpenes

Catalytically hydrogenisation of limonene
 hydratation of limonene:





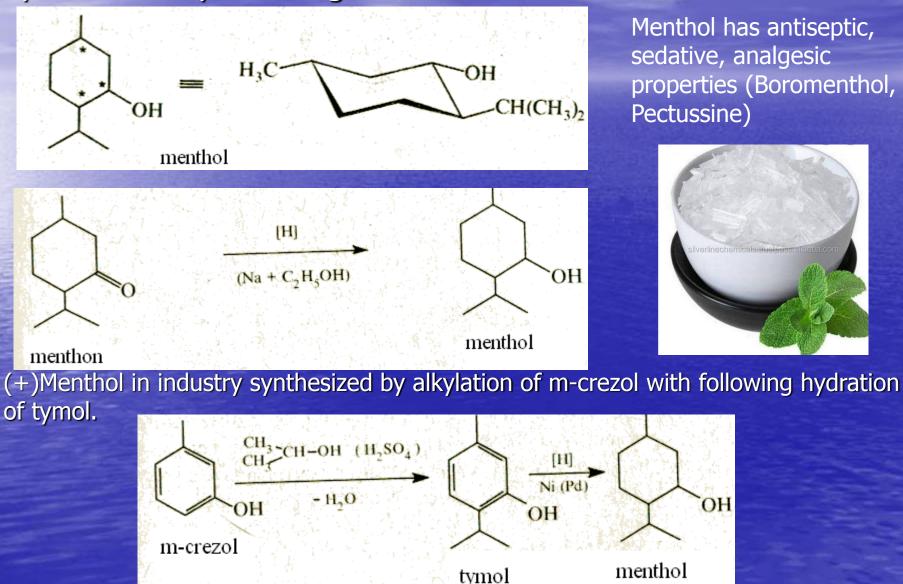


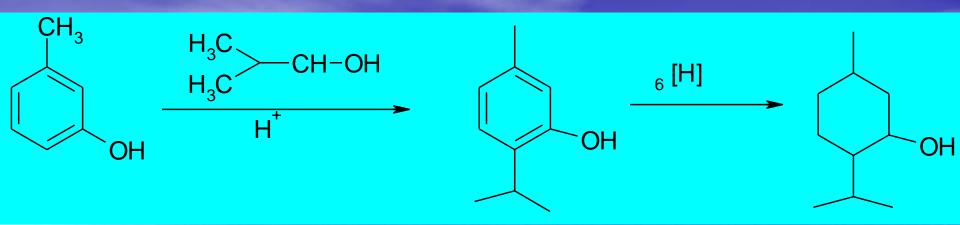
Menthane (1-isopropilmethylbenzol)

is obtained from p-cimol (n-isopropilmethylbenzol) hydration.

From hydroxyderivatives of menthane most important is menthol (menthanol-3), which has tree asymmetric centers. (-)Menthol synthesized by reducing of menthon.

OH





Meta-



A traditional bookbinder at work

thymol



Thymus

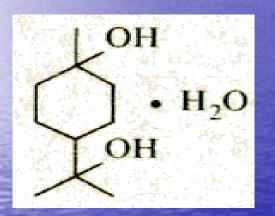
menthol

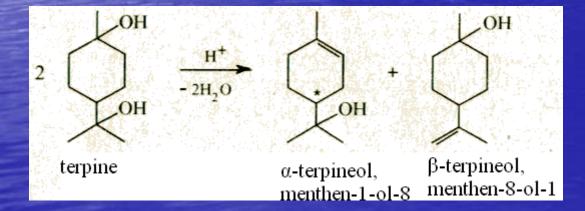




Mentha arvensis

Terpinehydrate (monohydrate menthandiol-1,8) use in medicine in treatment of chronic bronchitis.







Bicyclic monoterpenes:

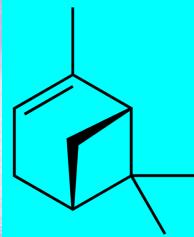
The same tertiary carbocation serves as the precursor to numerous bicyclic monoterpenes. A carbocation having a bicyclic skeleton is formed by intramolecular attack of the electrons of the double bond on the positively charged carbon. In the basis of bicyclic monoterpenes are four cyclic terpenic carbohydrates:

pinane; 2,6,6-trimethylbicyclo [3,1,1]heptane camphane; bornane; 1,7,7-trimethylbicyclo[2,2,1]heptane

carane; 4,7,7-trimethylbicyclo [4,1,0]heptane

thuyane; sabinane; 1-isopropile-4-methyl bicyclo[3,1,0]hexane

Pinenes

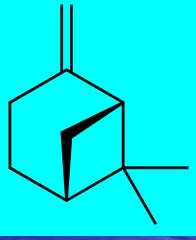


Alpha-pinene





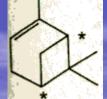
Resin of a pine



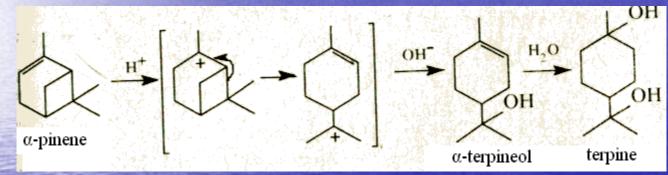
Beta-pinene

Pine

a-Pinene contains in turpentine oil – turpentine (up to 75 %).



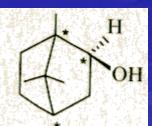
Heating with dilute acids (H2SO4, HNO3):

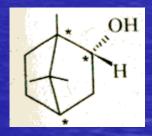


After oxidation on air forms verbenon:

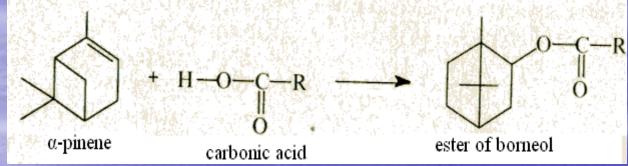
Borneol – alcohol of bornane (camphane) chain:

Isoborneol is borneol's diastereomer:

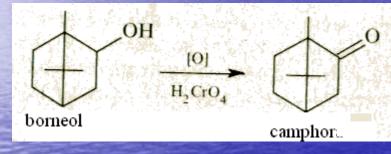




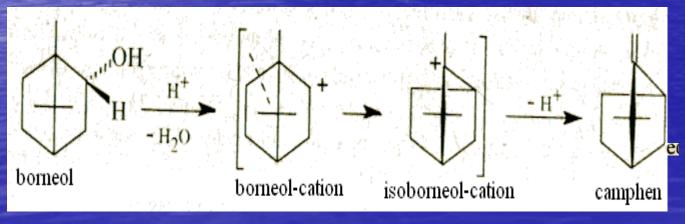
Synthesis of difficult esters of borneol



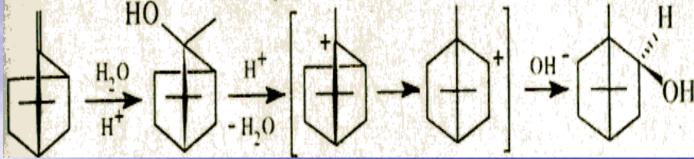
Oxidation by chromic acid:



Interaction between borneol and acids:

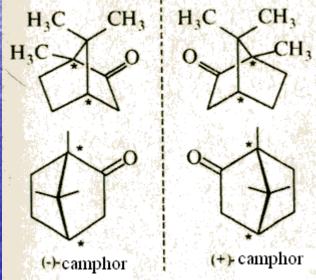


Camphene can hydrolyze in acidic medium with formation of isoborneol.



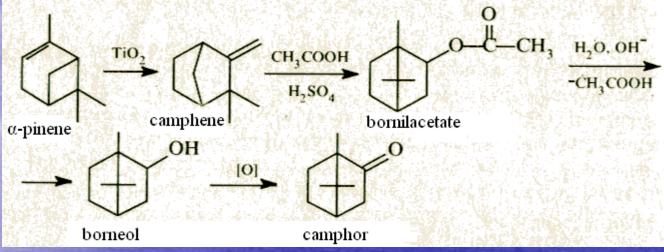
Camphor – bicyclic ketone,

has two asymmetric atoms, but dosen't have diastereomers.

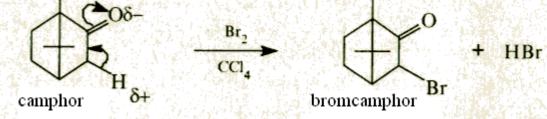


Camphor uses for stimulation of respiratory and vesselmoving centers, has antiseptic properties, stimulates metabolite processes.

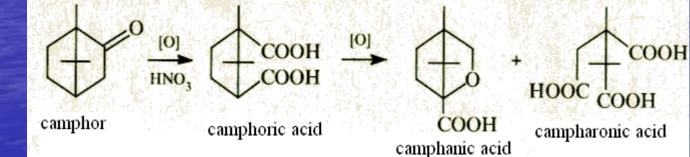
Tishchenko synthesis



Methylene group in a-location (according to carbonyl group) has CHacidic properties.



Oxidation of camphor with nitrate acid



Sesquiterpenes (C₁₅H₂₄)

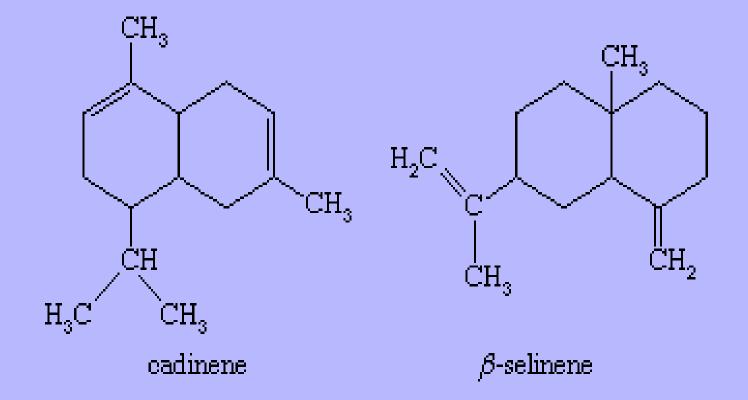


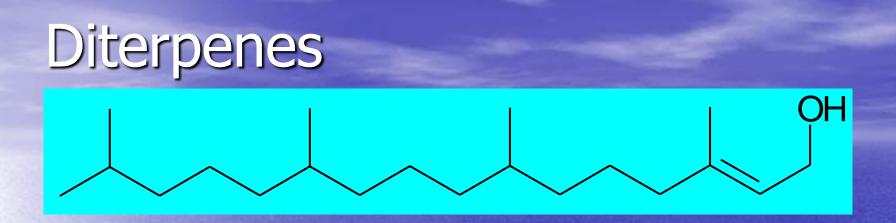




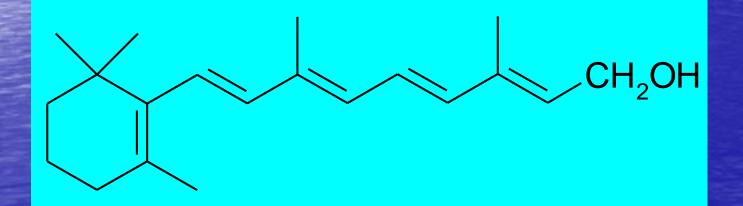
Lemon grass plant

Sesquiterpenes (C₁₅H₂₄)





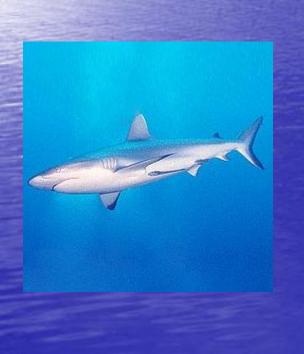
Phytol can be used as a precursor for the manufacture of synthetic forms of vitamin E and vitamin K1.



Retinol (Vit A)

Triterpenes (C₃₀H₄₈)

Squalene





Olive Tree



Moisturizer

Tetraterpenes

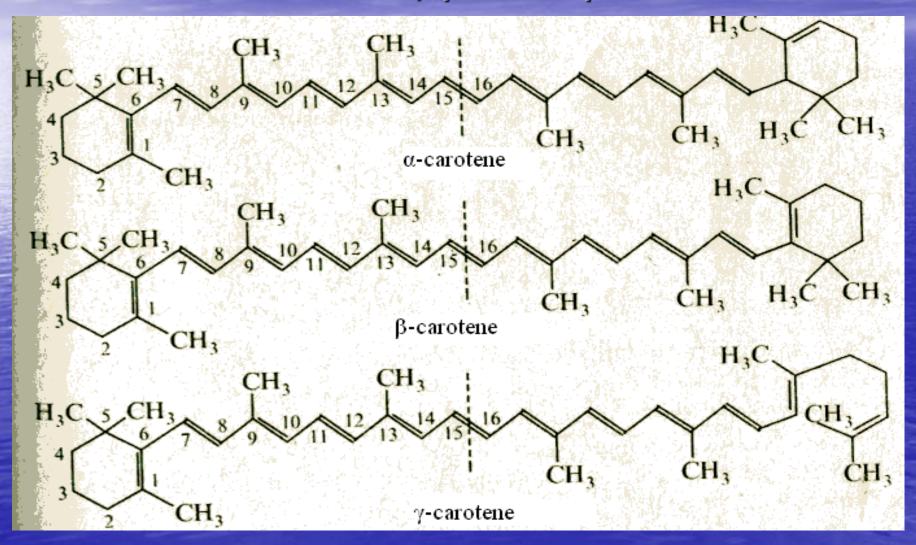


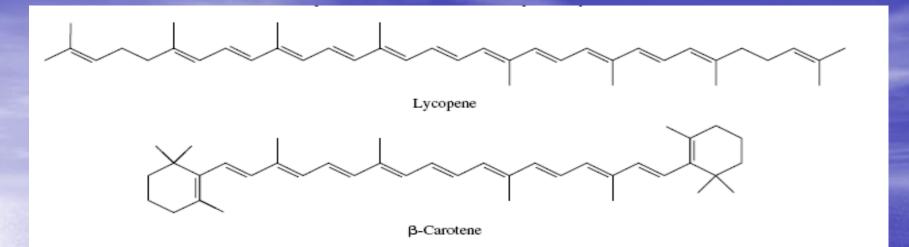
The term **carotene** (also **carotin**) is used for several related hydrocarbon substances having the formula C40H60, which are synthesized by plants but cannot be made by animals. Carotene is an orange photosynthetic pigment. They are responsible for the orange colour of the <u>carrot</u>, for which this class of chemicals is named, and for the colours of many other fruits and vegetables (for example, sweet potatoes and orange <u>cantaloupe</u> melon).

Carotenoids.

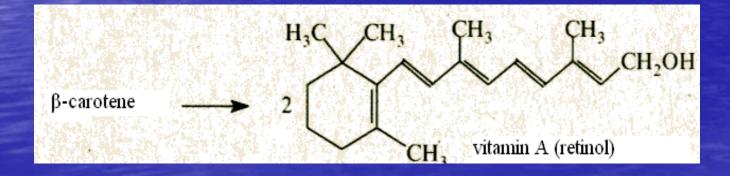
Carotenoids are natural pigments characterized by a tail-to-tail linkage between two C20 units and an extended conjugated system of double bonds. They are the most widely distributed of the substances that give color to our world and occur in flowers, fruits, plants, insects, and animals. It has been estimated that biosynthesis from acetate produces approximately a hundred million tons of carotenoids per year. The most familiar carotenoids are lycopene and -carotene, pigments found in numerous plants and easily isolable from ripe tomatoes and carrots, respectively.

Carotene – yellow-red pigment, contains in carrot, milk and butter. Carotene is a mixture of tree isomers – α-, β- and γ-carotene.





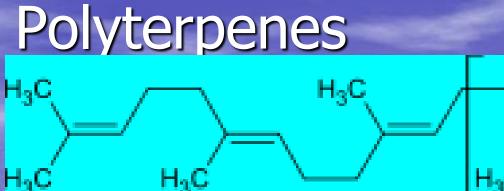
Carotenoids absorb visible light and dissipate its energy as heat, thereby protecting the organism from any potentially harmful effects associated with sunlight-induced photochemistry. They are also indirectly involved in the chemistry of vision, owing to the fact that -carotene is the biosynthetic precursor of vitamin A, also known as retinol, a key substance in the visual process.



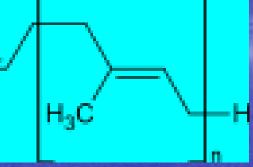


Lycopene works by quenching singlet oxygen which is produced during ultraviolet light and is responsible for skin cancer and ageing. Several lycopene clinical trials and studies in test tubes have shown many lycopene benefits including it to be 100 times more efficient at quenching singlet oxygen than Vitamin E. Lycopene has even been linked recently tohelping osteoporosis and male infertility. Potentially a anti-oxidant, anti-aging & anti-cancer supplement to be taken daily.





n=100





Palaquium gutta

Coagulated exudate isolated from several species of the tropical tree Palaquium (Sapotaceae). It is the transisomer of natural rubber and is used as a filling and impression material in dentistry and orthopedics and as an insulator in electronics. It has also been used as a rubber substitute.

